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Assessment of Hydriding in the U-Si System Title:

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Assessment of Hydriding in the U-Si System

Nuclear Technology Research and Development

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FCRD Program
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SUMMARY

Fuels with high uranium densities have been considered in the Nuclear Technology Research and Development program's Advanced Fuels Campaign as potential replacements for uranium(IV) oxide in commercial light water reactors. One such candidate fuel is U₃Si₂, which has been observed to readily oxidize and potentially hydride in steam and simulated pressurized water reactor conditions. The hydrogen absorption properties of U₃Si₂, in particular, are not well-understood.

Research this FY has focused on developing a better understanding of the hydrogen absorption characteristics of U₃Si₂ in steam and in pure hydrogen. Pellets of U₃Si₂ were exposed to 75% steam at various temperatures and monitored for mass changes using thermogravimetric analysis, while pellets and ingots exposed to pure hydrogen in a Sieverts' apparatus exhibited signs of hydrogen absorption. It was observed that hydrogen absorption of U₃Si₂ required higher pressures of hydrogen than those required to hydride uranium metal at similar temperatures.

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ACRONYMS

PWR	Pressurized water reactor
FRL	Fuels Research Laboratory

XRD

X-ray diffraction
Thermogravimetric analysis/analyzer
Hydrogen-to-uranium ratio
Pressure-composition-temperature
Powder diffraction file TGA

H/U

PCT

PDF

ASSESSMENT OF HYDRIDING IN THE U-SI SYSTEM

1. INTRODUCTION

Uranium silicides, such as U₃Si₂, are promising candidates for accident tolerant fuels because of their high thermal conductivities and uranium densities, as compared with UO₂. Higher thermal conductivity results in lower fuel centerline temperatures during operation and, thus, lower stored energy of the reactor core. Additionally, thermal conductivities of these compounds increase with temperature, which will help mitigate fuel rod damage during a reactivity-initiated accident such as a control rod ejection or a large break loss of coolant accident.

High uranium density results in an increased fission density and, thus, allows for a greater neutronic penalty from accident tolerant fuel claddings. Proposed accident tolerant claddings include stainless steel, Fe-Cr-Al (and derivative alloys), and silicon carbide because of their improved resistance to waterside corrosion compared to zirconium-based fuel cladding. However, all of these cladding concepts use elements with higher neutron absorption cross-sections than zirconium. Because of this, the improved fission density of uranium silicides enables the use of these types of cladding in reactors.

In addition to accident tolerance with respect to neutronics and thermal conductivity, it is important to assess the behavior of U_3Si_2 in a cladding breach scenario. However, resistance of uranium silicides to waterside corrosion during such conditions is not well-understood. In particular, U_3Si_2 exposed to high-temperature steam and simulated pressurized water reactor (PWR) environments has been observed to degrade by rapid pulverization.

Previous work in FY17 within the campaign examined the performance of U_3Si_2 in a variety of environments such as synthetic air (21% O_2 , balance Ar), 75% steam, high-temperature/pressure water with hydrogen water chemistry, and 6% H_2 /Ar (Wood et al., 2018; Nelson et al., 2018). These tests were carried out *in-situ* using thermogravimetric analysis in the cases of synthetic air, steam, and hydrogen and inautoclave for simulated PWR conditions.

Thermogravimetric analysis in steam and 6% H₂/Ar (Figure 1), as well as simulated PWR conditions (Figure 2), showed significant mass loss. For waterside corrosion, mass loss occurred over days, while in steam and hydrogen environments, mass loss occurred over the course of minutes to hours. Microstructural analysis of samples tested in these conditions showed evidence of an unidentified secondary phase and comparison with literature lead to the hypothesis that U₃Si₂ absorbs hydrogen to form a hydride phase that spalls off and exposes the corrosion medium to new surfaces. An example of the observed secondary phase in a steam-corroded samples is shown in Figure 3. The existence of a hydride phase was further supported by the calculation of a U₃Si₂H_{2-x} phase using density functional theory (DFT) methods (Mašková et al., 2017, p. 2; Middleburgh et al., 2018). The hydride phase studied in literature was formed at very high pressures of hydrogen (12 MPa) and varying temperature (between 25 and 500 °C during a temperature ramp and cooling) (Mašková et al., 2017, p. 2). Because the hydrides were formed under variable conditions, the hydrogen content of this phase and the conditions for producing it are not well-understood, especially as a function of temperature and hydrogen pressure.

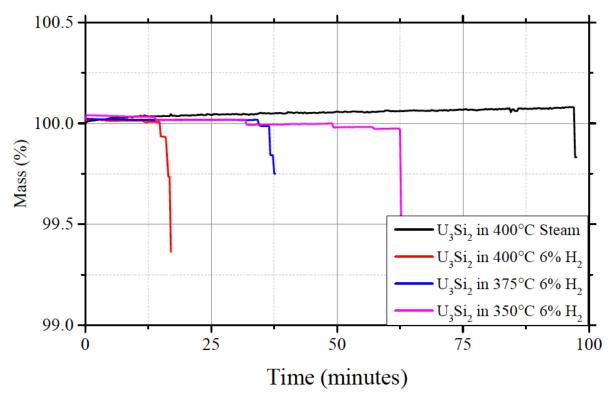


Figure 1: Isothermal exposures of U_3Si_2 pellets to flowing 6% H_2/Ar at 350 (magenta), 375 (blue), and 400 (red) °C. Isothermal data for U_3Si_2 in flowing steam at 400 °C is shown in black for comparison. Figure and caption adapted from (Wood et al., 2018).

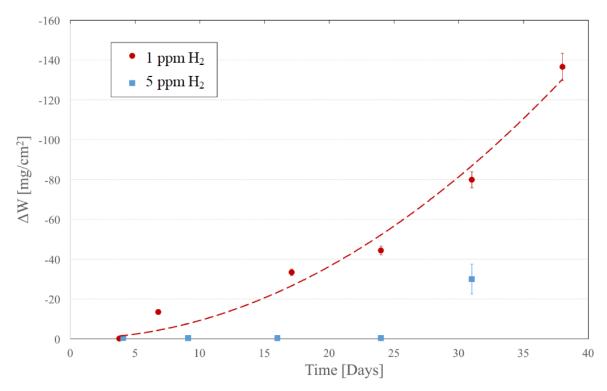


Figure 2: Weight change measured for U_3Si_2 samples as a function of exposure time at 300 °C for two different water chemistry conditions. Error bars represent average of multiple samples and standard error of measurement technique. A trend line is added to the 1-ppm H_2 sample data to guide the eye. Samples tested at 6-ppm H_2 fully pulverized when examined after 38 days so measurement was not possible. Figure and caption adapted from (Nelson et al., 2018).

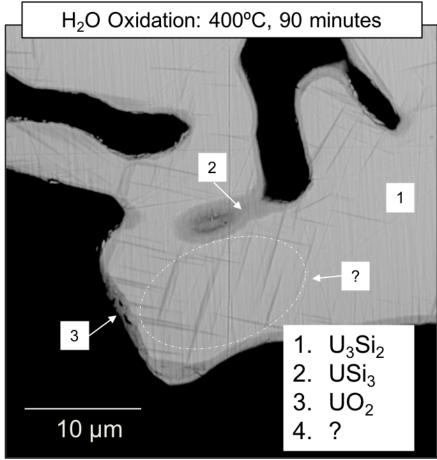


Figure 3: Micrograph taken from a cross-sectioned U₃Si₂ pellet exposed to steam at 400 °C. Pellet was exposed for 1.5-hr. Unknown phase is hypothesized to be hydride-phase lamellae. Figure and caption adapted from (Wood et al., 2018).

This work represents a continuation of work previously performed at LANL with the specific focus on the hydriding aspects of U_3Si_2 . In this study, a two-pronged approach to understanding U_3Si_2 hydriding was taken: steam oxidation tests were conducted on U_3Si_2 pellets of well-defined geometry to determine whether the onset of hydriding from a temperature standpoint could be measured while hydrogen absorption experiments using a Sieverts' apparatus were conducted on U_3Si_2 pellets and button fragments to measure the maximum amount of hydrogen that can be absorbed by U_3Si_2 and the hydrogen pressures required to form the hydride phase. X-ray diffraction (XRD) was also used in an attempt to understand the structure of the hydride phase.

2. Experimental methods

2.1 Materials

Buttons of U₃Si₂ were synthesized by arc-melting the pure elements together in an inert, argon glovebox with oxygen and water contamination levels maintained below 0.1 ppm. Uranium metal was obtained from AeroJet Rocketdyne (Jonesborough, TN), while silicon chips were obtained from Cerac, Inc. (now Materion). Masses of uranium and silicon were measured out to match the 3:2 mole ratio in U₃Si₂.

Powder processing of U_3Si_2 was performed in a high-purity argon glovebox line to minimize oxidation of powders. Phase-pure buttons, as confirmed via XRD, were crushed using a high-energy ball mill (SPEX) with 0.25 wt. % ethylene bis(stearamide) (EBS) binder for 30 minutes and subsequently sieved through a -325 mesh sieve (44 μ m). Pellets of U_3Si_2 were pressed at 150 MPa using a 5.2-mm punch and die set so as to form approximately 5-mm OD \times 2-mm thickness pellets post-sintering. These green bodies were then sintered at 1460 °C for 12-hours in gettered argon in a W-mesh furnace. Sintered pellet densities were measured using geometric methods and pellets were found to be between 81 - 87% of the theoretical density of U_3Si_2 . Because dimensions were measured for density calculations, these values are considered to be conservative estimates of density. However, for this set of corrosion and gas-absorption experiments, kinetics were not of importance, so well-characterized surface areas were not necessary and lower densities were preferred to yield faster reaction rates.

2.2 Steam corrosion testing

A simultaneous thermal analyzer (STA 449 F3, Netzsch Instruments, Selb, Germany) with a water vapor furnace and water vapor generator (DV2ML, Astream, Germany) was used to perform steam corrosion tests of U₃Si₂ pellets and measure mass change as a function of exposure time *in situ* at various temperatures. Pellets were placed in an alumina crucible to contain pulverized pellets during exposure and sample temperature was monitored using a type-S thermocouple. An image of the steam corrosion setup is shown in Figure 4.

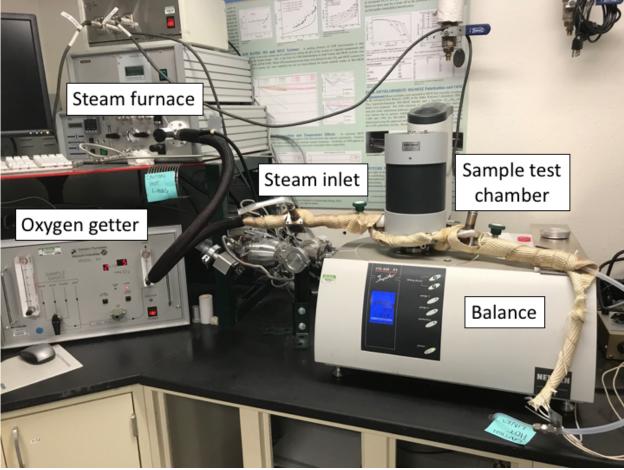


Figure 4: Experimental setup for steam TGA analysis. Annotations indicate major components of the system.

Samples were ramped up to testing temperatures in gettered argon at 10 °C/min and allowed to stabilize at the test conditions for 30-min before introduction of steam. For all tests, the water vapor flowrate was varied to maintain a consistent steam fraction of the gas depending on the testing temperature. Gettered argon at 8 L/hr (calibrated with nitrogen) acted as a carrier gas for the steam, while a protective gas of gettered argon at 20 mL/min was purged through the balance during each run. Samples were held at temperature under steam conditions for 10-hr.

2.3 Sieverts' gas absorption

U₃Si₂ pellets and button fragments were loaded in a stainless-steel reaction vessel inside an inert glovebox. The reaction vessel was attached to a gas manifold and then placed inside a tube furnace to maintain temperature. All manifold connections were composed of Swagelok VCR fitting using silver-plated nickel gaskets to provide a leak-tight seal. The whole system was evacuated and then the reaction chamber was brought to temperature. System pressure was measured using a Heise ATS 2000 0-200 psia pressure transducer, which measures absolute pressure, rather than gauge pressure. An annotated image of the Sieverts' apparatus is shown in Figure 5.

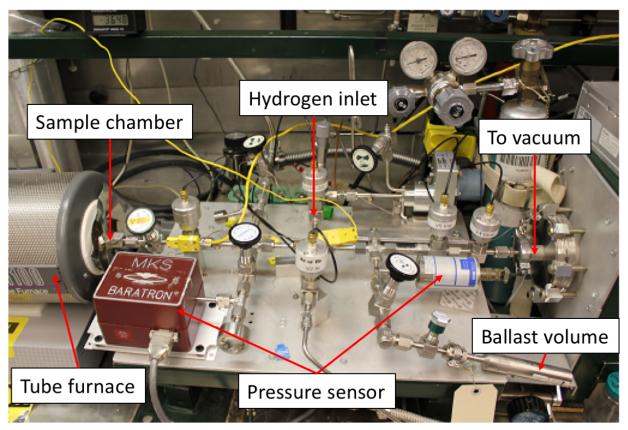


Figure 5: Experimental apparatus for Sieverts' gas absorption. Important components of the apparatus are annotated.

Volume calibration was performed using a 52.67-mL calibrated expansion volume. The calibrated volume was filled with a known pressure of helium gas and then opened to the manifold and the sample reaction chamber. The manifold and reaction chamber volumes were then calculated using Boyle's Law $(P_1V_1 = P_2V_2)$. This process was performed four times to calculate average values for the relevant volumes.

Hydrogen dosing was performed by injecting a known pressure of hydrogen. Once the pressure had equilibrated within the manifold, the valve to the reaction chamber was opened and the gas allowed to equilibrate in the reaction chamber. Equilibration in the reaction chamber was due to gas expansion into the increased volume and absorption of hydrogen by the sample. The gas pressure was allowed to equilibrate for one hour, after which the sample chamber was isolated from the manifold and gas was aliquoted again and the process repeated. Measurements were terminated once the system reached a pressure value that was pre-defined in the experiment definition. Hydrogen aliquoting was controlled using a LabView program based off readings from the Heise pressure transducer.

Moles of gas absorbed were calculated from the ideal gas law using aliquot pressures and volumes and reaction equilibrium pressures and volumes. These were then compared with the initial moles of uranium in U_3Si_2 to calculate the hydrogen-to-uranium (H/U) ratio. After testing, samples were sealed in the reaction vessel and transferred to sample storage vials in an inert glovebox with oxygen levels maintained below 1-ppm to minimize degradation of the hydrided U_3Si_2 .

2.4 Microstructural analysis

XRD was used to confirm the composition of the initial U_3Si_2 buttons and to also analyze the hydrided U_3Si_2 . A Bruker XRD (D2 Phaser, Bruker AXS, Madison, WI, USA) was used for these analyses.

Compositional analyses of buttons were performed with quick XRD scans with 2θ ranging between 10 and 90° with a 0.02° 2θ step and a 2-s acquisition time for each step. Hydride phase analysis was performed using longer scans with the same 2θ range but a 2θ step size of 0.01° and 5-s acquisition time. Material for all XRD examinations were homogenized using a mortar and pestle in an inert, argon glovebox and encapsulated in a low-background XRD sample holder to prevent exposure to air.

3. Results and discussion

3.1 Steam corrosion testing

As mentioned earlier, pellets of U_3Si_2 were exposed to steam at various temperatures to determine the onset of hydriding. To do this, mass change was measured as a function of exposure time and degradation mechanism was noted (i.e. ejection of pellet fragments vs. pulverization). Mass change (in percent) as a function of exposure time for each testing temperature is shown in Figures 6 - 9. Testing temperatures were 250 °C (Figure 6), 300 °C (Figure 7), 350 °C (Figure 8), and 500 °C (Figure 9). Inset in each of these figures is the physical appearance of the sample after testing. It should be noted that large spikes in mass change in these figures are an artifact of the steam generator, rather than physical mass changes.

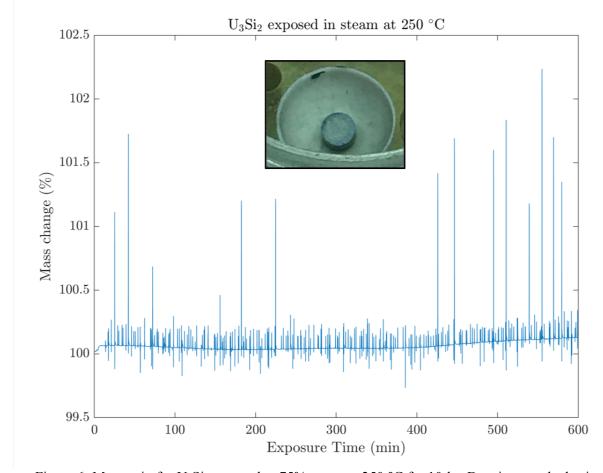


Figure 6: Mass gain for U_3Si_2 exposed to 75% steam at 250 °C for 10-hr. Data is smoothed using a moving average filter with moving average span of 5. In the inset is an image of the sample post-testing.

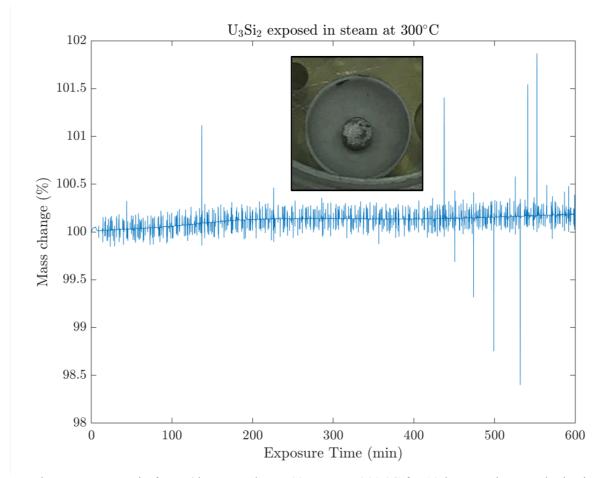


Figure 7: Mass gain for U_3Si_2 exposed to 75% steam at 300 °C for 10-hr. Data is smoothed using a moving average filter with moving average span of 5. In the inset is an image of the sample post-testing.

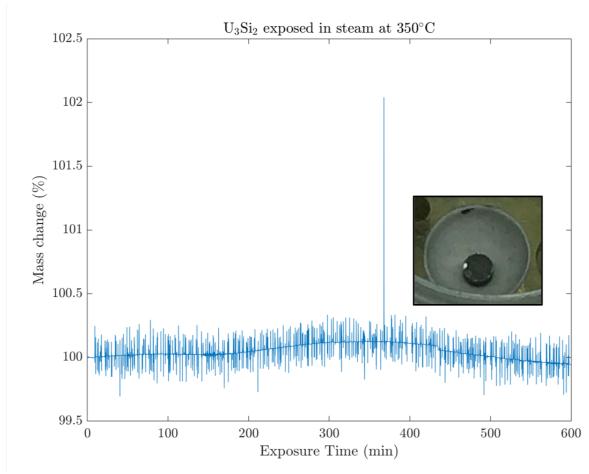


Figure 8: Mass gain for U_3Si_2 exposed to 75% steam at 350 °C for 10-hr. Data is smoothed using a moving average filter with moving average span of 5. In the inset is an image of the sample post-testing.

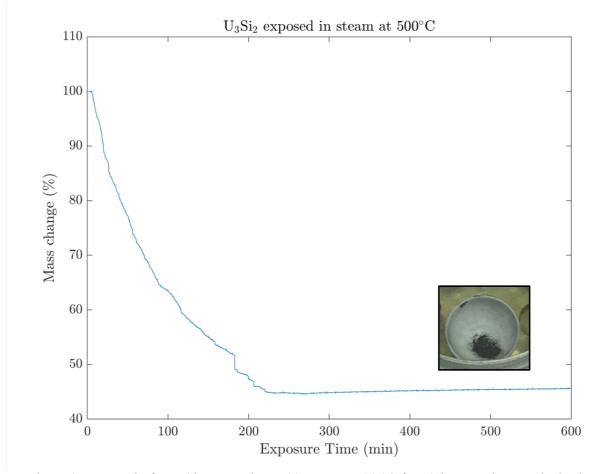


Figure 9: Mass gain for U₃Si₂ exposed to 75% steam at 500 °C for 10-hr. Data is smoothed using a moving average filter with moving average span of 5. In the inset is an image of what remained of the sample post-testing.

Figure 6 shows that, in 75% steam at 250 °C, U_3Si_2 did not seem to change appearance with exposure time and mass change was minimal, though a slight color change was noted. Very small mass changes were also observed for steam testing at 300 (Figure 7) and 350 (Figure 8) °C, though the inset images show the slow development of oxide on the surface, with the surface of the sample tested at 350 °C almost fully covered by an oxide layer. Figure 9 shows the mass change as a function of exposure time for U_3Si_2 in 75% steam at 500 °C. For this test, mass was observed to consistently decrease as a function of time. This was not due to actual mass change of the sample, but rather ejection of pellet fragments during oxidation testing. The end result of this test was an inactive, black powder (shown in the inset of Figure 9), which is consistent with observations in previous work and measurement of U_3O_8 . Another test performed at 700 °C exhibited rapid mass loss in the absence of steam and a large temperature increase upon addition of steam (large enough to soft-reset the instrument). The sample condition after testing is shown in Figure 10, which indicates partial oxidation of the pellet and spalled oxide.

Comparison of mass changes for the low-temperature tests (250, 300, and 350 °C) is shown in Figure 11. Data is severely smoothed and is only used to compare general trends in mass change. This comparison shows that, at both 250 and 300 °C, U₃Si₂ appeared to gain a very small amount of mass, though it is not clear whether this was from oxidation, hydrogen absorption, or an artifact of the technique due to baseline drift. Previous work on U₃Si₂ in steam at similar temperatures resulted in samples described as having no mass change or structural degradation, so it is still unclear what the cause of the measured mass changes might be. While the sample exposed at 250 °C exhibited no clear oxide scale, the surface of the sample

exposed at 300 °C displayed small patches of oxide, which is consistent with measured mass gain in Figure 11. Beyond approximately 400 minutes, mass change for U_3Si_2 exposed at 350 °C shows a very slight mass decrease. Because of the presence of black-colored powder on the instrument fixturing after the corrosion test, it is hypothesized that 350 °C is near the temperature where U_3Si_2 begins to degrade and fall apart in steam. Figure 12 shows a comparison between all steam corrosion data sets and is primarily to highlight the extent of mass loss at high temperature due to ejection of sample fragments during testing.



Figure 10: U₃Si₂ exposed to 75% steam at 700 °C. Corrosion test lasted only a few seconds before the temperature spike due to oxidation caused a soft reset of the instrument.

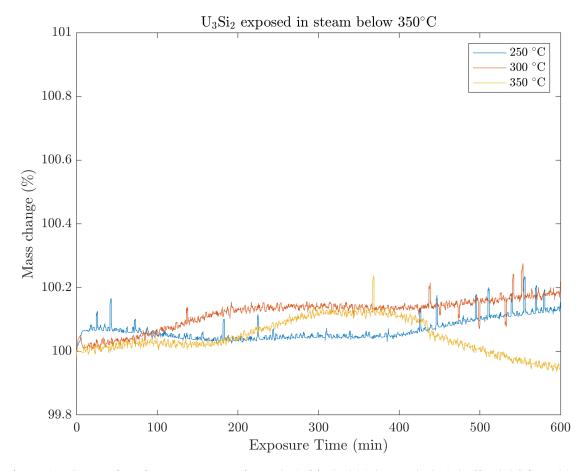


Figure 11: Comparison between mass gains at 250 (blue), 300 (orange), 350 (yellow) °C in 75% steam. Data is smoothed to show general trends in mass change, only, and is not considered analytical.

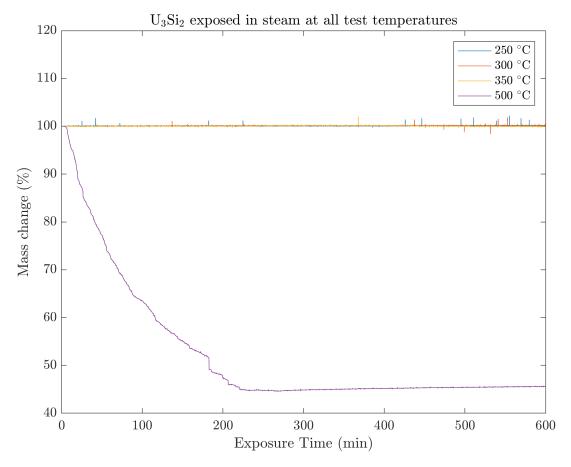


Figure 12: Comparison between mass gains at 250 (blue), 300 (orange), 350 (yellow), and 500 (purple) °C in 75% steam. Data is smoothed using a moving average filter with moving average span of 5.

In FY17 work, it was hypothesized that the hydriding could be separated from oxidation by determining the limits of stability for the U_3Si_2 hydride during steam oxidation tests. From these results, it is clear that, using thermogravimetry alone, it is not possible to determine the regimes of stability for U_3Si_2 hydriding versus oxidation in steam. At low temperatures, U_3Si_2 was not observed to change mass significantly, whereas, at high temperatures, the oxidation reaction occurred so rapidly that it was difficult to determine whether oxidation or hydriding were the dominant degradation mechanisms. Hydriding could not be fully ruled out because mass changes due to absorption of hydrogen are small: fully hydriding U_3Si_2 to UH_3 will result in a mass change of approximately 1.2% and decoupling this from mass change due to oxidation is very difficult. Based on the difficulty of such an analysis, it was concluded that steam oxidation testing of U_3Si_2 at elevated temperatures would not aid in assessing hydriding and corrosion performance.

3.2 Sieverts' gas absorption

For hydrogen absorption experiments, samples of U_3Si_2 , both pellets and button fragments, were placed in a stainless-steel reaction chamber, which was connected to a gas manifold and then placed inside a tube furnace to maintain testing temperature. Hydrogen was added to a known pressure in the manifold with a known volume. From this the initial moles of hydrogen were calculated using the ideal gas law. The sample chamber was opened to the manifold, allowing the gas to flow into the sample chamber. The pressure was allowed to equilibrate for one hour and then measured. From this, the final number of hydrogen moles in the gas phase was determined. Using both initial and final moles of hydrogen, the amount of hydrogen

absorbed by the sample was able to be calculated and then converted to a hydrogen-to-uranium atomic ratio based on the initial mass of uranium in the U₃Si₂ sample.

From these data, a pressure-composition isotherm for U_3Si_2 was able to be calculated for each temperature, as shown in Figure 13 at 350 °C, which plots equilibrium pressure of hydrogen as a function of the hydrogen-to-uranium ratio.

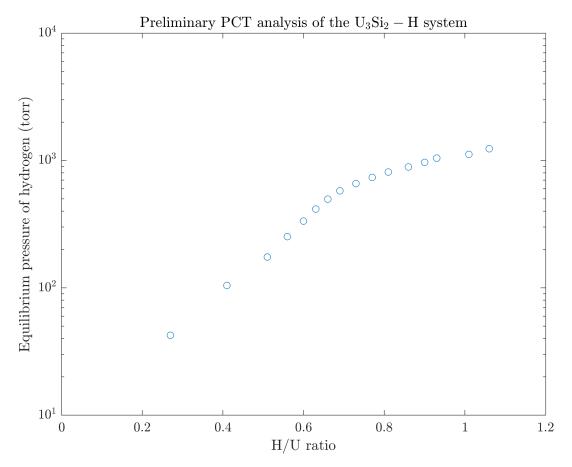


Figure 13: Preliminary pressure-composition-isotherm for U₃Si₂ in hydrogen at 350 °C. Final H/U ratio was calculated to be 1.06.

Preliminary data studying the U_3Si_2-H system at 350 °C is plotted in Figure 13. In this plot, the initial, sloped rise in hydrogen pressure is attributed to accommodation of hydrogen in the U_3Si_2 lattice as solid-solution atoms. After the initial increase in hydrogen pressure, there is typically a plateau region where aliquoting more hydrogen would result in the same pressure of hydrogen; such a plateau region would indicate the transformation of U_3Si_2 with hydrogen in solid-solution to a true hydride phase. The pressure-composition isotherm in Figure 13 for 350 °C does not exhibit a true plateau region, which implies that increasing hydrogen pressures are needed to drive further hydrogen absorption in U_3Si_2 . This particular sample was exposed to hydrogen up to a calculated H/U ratio of 1.06.

The pressure of hydrogen required to hydride U_3Si_2 (up to 1200 torr in Figure 13) is much higher than those required to hydride pure uranium (350 torr at 350 °C). Two possible explanations for this are that (1) the silicon in U_3Si_2 presents a barrier to hydrogen absorption and that, upon hydriding, U_3Si_2 separates to UH₃ and Si or (2) U_3Si_2 hydrides to a separate phase, $U_3Si_2H_x$, as has been proposed in literature.

Microstructural analysis of U₃Si₂ hydrided to termination has yet to be done, but would provide evidence for either explanation.

3.3 Microstructural analysis

XRD was performed on U_3Si_2 exposed to hydrogen at 860 torr and 400 °C. Results were compared with the Powder Diffraction File (PDF) for U_3Si_2 , as well as XRD data from previous work on U_3Si_2 exposed in 6% H_2 /Ar for 50-hr and literature data of $U_3Si_2H_{1.8}$. This comparison is plotted in Figure 14.

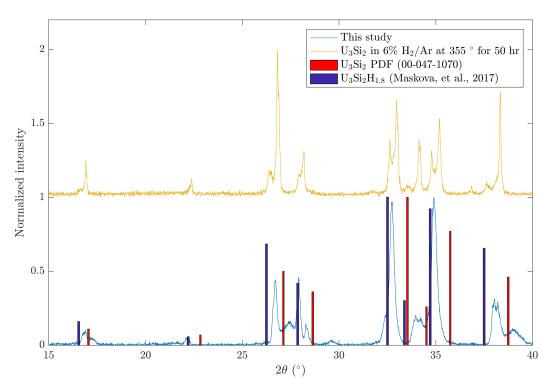


Figure 14: XRD pattern collected from U₃Si₂ exposed to hydrogen gas at 860 torr and 400 °C. Data from this study is shown in blue, while data from exposure of U₃Si₂ to flowing 6% H₂/Ar at 355 °C for 50-hr from (Wood et al., 2018). Red bars indicate the PDF peak indices for U₃Si₂, while blue bars indicate peak indices for U₃Si₂H_{1.8} from (Mašková et al., 2017, p. 2).

The results from this work are shown in blue lines, while the results from exposure in 6% H₂/Ar are shown in yellow (offset). Red bars represent peak indices from the PDF for U₃Si₂, while blue bars represent peak indices for U₃Si₂H_{1.8} from literature (Mašková et al., 2017, p. 2). Figure 14 shows that the peaks associated with U₃Si₂ hydrided at 400 °C are shifted to lower 20 than for pure U₃Si₂, but higher 20 than for U₃Si₂H_{1.8}. Because the diffraction peaks are simply shifted to lower 20 as compared with the PDF for U₃Si₂, it is hypothesized that all of the hydrogen in the sample was entirely in solid-solution. This would result in an expansion of the U₃Si₂ lattice and, thus, a shift in XRD pattern peak position to lower 20 (higher d-spacing). This is in contrast with the diffraction pattern, taken from (Wood et al., 2018), for U₃Si₂ in 6% H₂/Ar, which has shoulder peaks at the indices for U₃Si₂H_{1.8} and larger peaks at the indices for U₃Si₂, which could indicate phase separation in the sample. Hydrogen absorption to termination of hydriding should be performed and the sample analyzed via XRD for confirmation of the U₃Si₂H_{1.8} structure.

4. Summary and future work

Steam corrosion and hydriding performance of U₃Si₂ were studied using steam-coupled thermogravimetry and Sieverts' gas absorption, respectively. Steam oxidation results showed that U₃Si₂

does not appreciably degrade below 350 °C and that, above this temperature, rapid ejection of sample fragments occurs. It was determined that it was difficult to decouple hydriding from oxidation due to the rapidity of oxidation and fragment ejection. Hydrogen absorption results showed that U_3Si_2 requires much higher pressures of hydrogen to absorb it than does pure uranium metal. U_3Si_2 was hydrided to H/U ratios of 1.06 at 350 °C, though hydriding was not performed to termination. Preliminary results suggest that this would require hydrogen pressures much higher than what was achieved in this study.

Future experiments studying hydriding of U_3Si_2 will focus on higher pressures of hydrogen to drive the hydrogen absorption reaction to termination, when the hydrogen pressure will rapidly increase with little absorption of hydrogen. This will be further expanded by studying hydriding at higher temperatures and attempt to understand conditions where U_3Si_2 hydriding might be unfavorable during cladding-breach conditions based on gas absorption experiments. Analysis of the plateau pressures for hydriding will also enable the calculation of the formation enthalpy and entropy of the hydride, as well as formation enthalpies for various $U_3Si_2 - H$ compounds, which will provide fundamental thermodynamic properties of this newly-identified phase. Future work will focus on coupling Sieverts' gas absorption-type experiments with thermogravimetric analysis to determine degradation mechanisms of prospective LWR fuels.

5. Bibliography

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